



# Hydrocarbon superhydrophobic polymers from electrochemical polymerization: an alternative to fluorine?

Mélanie Wolfs

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UNIVERSITE DE NICE-SOPHIA ANTIPOLIS - UFR Sciences  
Ecole Doctorale « Sciences Fondamentales et Appliquées »

## THÈSE

pour obtenir le titre de

Docteur en Sciences  
de l'UNIVERSITE de Nice-Sophia Antipolis

Discipline : Chimie

Présentée et soutenue par

**Mélanie WOLFS**

### **HYDROCARBON SUPERHYDROPHOBIC POLYMERS FROM ELECTROCHEMICAL POLYMERIZATION: AN ALTERNATIVE TO FLUORINE?**

Thèse dirigée par le Professeur Frédéric GUITTARD et le Docteur Thierry DARMANIN

Soutenue le 13 / 12 / 2013 devant le Jury composé de

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## Glossary

|   |   |
|---|---|
| AAO   | Anodic Aluminum Oxide   |
| AFM   | Atomic Force Microscopy   |
| Bu <sub>4</sub> NBF <sub>4</sub>                                | Tetrabutylammonium tetrafluoroborate  |
| Bu <sub>4</sub> NC <sub>4</sub> F <sub>9</sub> SO <sub>3</sub>  | Tetrabutylammonium nonafluorobutanesulfonate                                  |
| Bu <sub>4</sub> NC <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> | Tetrabutylammonium heptadecafluorooctanesulfonate                             |
| Bu <sub>4</sub> NCF <sub>3</sub> SO <sub>3</sub>                | Tetrabutylammonium trifluoromethanesulfonate                                  |
| Bu <sub>4</sub> NCIO <sub>4</sub>                               | Tetrabutylammonium perchlorate  |
| Bu <sub>4</sub> NPF <sub>6</sub>                                | Tetrabutylammonium Hexafluorophosphate  |
| CV  | Cyclic Voltammetry  |
| d   | Doublet   |
| dd  | Doublet of doublet  |
| DMAP  | 4-(dimethylamino)pyridine   |
| DMF   | Dimethylformamide   |
| E <sub>1/2</sub>  | Half-wave potential   |
| ECA   | ethyl-cyanoacrylate   |
| EDC   | <i>N</i> -(3-dimethylaminopropyl)- <i>N</i> '-ethylcarbodiimide hydrochloride |
| EDOT  | 3,4-Ethylenedioxythiophene  |
| EOTT  | 3,4-Ethyleneoxythiathiophene  |
| EOTT  | 3,4-ethyleneoxythiathiophene  |
| E <sup>ox</sup>   | Monomer oxidation potential   |
| E <sub>ox, polym</sub>  | Polymer oxidation potential   |
| E <sub>ox</sub>   | Monomer oxidation potential   |

|                         |   |
|-------------------------|---|
| $E_{\text{ox,opt}}$     | Optimal oxidation potential                       |
| $E_{\text{red, polym}}$ | Polymer Reduction Potential                       |
| GC-MS                   | Gas Chromatography coupled with Mass Spectroscopy |
| $H_{\text{liquid}}$     | Hysteresis measured with liquid droplet           |
| HDPE                    | High Density Poly(ethylene)                       |
| HFDT                    | Heptadecafluoro-1-decanethiol                     |
| J                       | Coupling Constant                                 |
| LbL                     | Layer-by-Layer                                    |
| LDPE                    | Low Density Poly(ethylene)                        |
| m                       | Multiplet   |
| m.p.                    | Melting point                                     |
| $\text{NaClO}_4$        | Sodium perchlorate                                |
| NMR                     | Nuclear Magnetic Resonance                        |
| PAA                     | Poly(acrylic acid)                                |
| PAN                     | Polyacrylonitrile                                 |
| PANI                    | Polyaniline                                       |
| PC                      | Polycarbonate                                     |
| PCL                     | Polycaprolactone                                  |
| PDMS                    | Poly(dimethylsiloxane)                            |
| PE                      | Polyethylene                                      |
| PECA                    | Poly(ethyl-cyanoacrylate)                         |
| PEDOT                   | poly(3,4-ethylenedioxythiophene)                  |
| PEDOT                   | Poly(3,4-ethylenedioxythiophene)                  |
| PEI                     | Poly(ethyleneimine)                               |
| PEOT                    | poly(3,4-ethyleneoxythiathiophene)                |
| PET                     | Polyethylene terephthalate                        |

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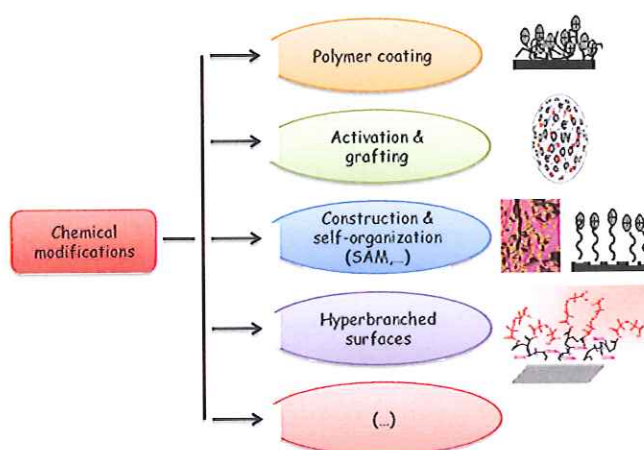
|                  |  |
|------------------|--|
| PFDA             | Poly(heptadecafluorodecylacrylate)                       |
| PFO <sup>-</sup> | Perfluorooctanoate anion                                 |
| PFTDS            | <i>1H,1H,2H,2H</i> -perfluorodecyltrichlorosilane        |
| PHFMA            | Poly(2,2,3,4,4,4-hexafluorobutyl methacrylate)           |
| PMETAC           | Poly[2-(methacryloyloxy)ethyltrimethylammonium chloride] |
| PMMA             | Poly(methyl methacrylate)                                |
| PNIPAAm          | Poly(N-isopropylacrylamide)                              |
| POSS             | Polyhedral oligomeric silsesquioxane                     |
| PP               | Poly(propylene)  |
| PProDOT          | Poly(3,4-propylenedioxythiophene)                        |
| PProDOP          | Poly(3,4-propylenedioxy pyrrole)                         |
| PS               | Poly(styrene)  |
| Pt               | Platinum   |
| PTFE             | Poly(tetrafluoroethylene)                                |
| pTSA             | <i>p</i> -toluenesulfonic acid                           |
| PU               | Polyurethane   |
| PUA              | Polyurethane acrylate                                    |
| PVC              | Poly(vinyl chloride)                                     |
| PVDF             | Poly(vinylidene fluoride)                                |
| PVDMA            | Poly(2-vinyl-4,4-dimethylazlactone)                      |
| Qs               | Deposition charge  |
| r                | Wenzel Roughness factor                                  |
| r.t.             | Retention time   |
| R <sub>a</sub>   | Arithmetic Roughness                                     |
| R <sub>q</sub>   | Root Mean Square Roughness                               |
| s                | Singlet  |

|                          |   |
|--------------------------|---|
| SCE                      | Saturated Calomel Electrode                                 |
| SEM                      | Scanning Electron Microscopy                                |
| sept.                    | Septuplet   |
| sext.                    | Sextuplet   |
| SI-ATRP                  | Surface-Initiated Atom Transfer Radical Polymerization      |
| t                        | Triplet   |
| TEOS                     | Tetraethyl orthosilicate                                    |
| THF                      | Tetrahydrofuran   |
| tt                       | Triplet of triplet  |
| UV                       | Ultra-violet  |
| $\alpha_{\text{liquid}}$ | Sliding angle measured for liquid                           |
| $\gamma_{\text{LV}}$     | Interfacial tension between Liquid-Vapor                    |
| $\gamma_{\text{SL}}$     | Interfacial tension between Solid-Liquid                    |
| $\gamma_{\text{SV}}$     | Interfacial tension between Solid-Vapor                     |
| $\delta$                 | Chemical shift  |
| $\theta_a$               | Advancing angle   |
| $\theta^{\text{CB}}$     | Apparent contact angle determined by Cassie-Baxter equation |
| $\theta_{\text{diiodo}}$ | Static diiodomethane contact angle                          |
| $\theta_r$               | Receding angle  |
| $\theta^{\text{W}}$      | Apparent contact angle determined by Wenzel equation        |
| $\theta_{\text{water}}$  | Static water contact angle                                  |
| $\theta_{\text{water}}$  | Water contact angle   |
| $\theta^{\text{Y}}$      | Contact angle of Young's equation                           |
| $\phi_a$                 | Air Fraction  |
| $\phi_s$                 | Solid fraction  |



# Introduction

From a chemist's point of view, making an hydrophobic surface is possible by using an hydrophobic bulk or by making surface modifications such as coating the surface with a polymer, activating and grafting hydrophobic molecules onto the surface, making self-assembled monolayers onto the surface or depositing self-assembled monolayers or hyperbranched polymers for example (Figure 1). With all these techniques, hydrophobic surfaces are mainly flat.



**Figure 1.** Examples of chemical modifications to produce hydrophobic surfaces.

The hydrophobicity comes from the intrinsic hydrophobicity of the bulk or the deposited species. The water-repellency is evaluated by measuring the contact

angle between the water droplet's tangent and the solid surface's tangent. With these techniques described in Figure 1, the highest water contact angle we could obtain was  $120^\circ$  which corresponds to the smooth surface of poly(tetrafluoroethylene) (PTFE). In 2000, Genzer and his co-workers previously stretched their surface before grafting a self-assembled monolayer of fluorinated compounds (Genzer, J; Efimenko, K. *Science* **2000**, *290*, 2130-2133). From this technique, they deposited a mechanically assembled monolayer (MAM) instead of a self-assembled monolayer (SAM). Thus, they enhanced the density of the grafted molecules and they increased the water-repellency with a water contact angle of  $130$ - $135^\circ$ .

Fluorinated compounds are often employed to fabricate hydrophobic surface. The advantages are their chemical and thermal inertia as well as their low surface energy. However due to their chemical inertia, long fluorinated tails are not easily degradable. As a consequence, it is very difficult or quasi impossible for the body of living species to eliminate these compounds. Long fluorinated tails are thus considered as bioaccumulable species. In opposition to synthetic pathway proposed in literature, in nature, we can find surfaces with extreme water-repellency properties (i.e. on which water droplets remained spherical) without

using fluorine chemistry. These surfaces are named superhydrophobic. This phenomenon could be explained by an appropriate combination of either morphology, either roughness or surface structuration and low surface energy raw materials. Hence, the main subject of this research work was to find alternative to fluorine chemistry by the preparation of superhydrophobic material within hydrocarbon series.

In literature, several techniques to produce superhydrophobic surfaces have been described. Amongst them, electrochemical polymerization allowed the design of surfaces with special wettability and especially the possibility to obtain superhydrophobic surfaces. The main advantages of this technique are:

- The speed: the deposition and the surface structuration occur at the same time
- The versatility: an accurate design of the monomer chemical structure influences the resultant morphology and properties. it is also possible to control the morphology through the electrochemical parameters (deposition charge, supporting electrolyte, solvent, deposition technique, etc)

In this thesis, the challenges were:

1. To make an assessment of the existed techniques to produce superhydrophobic surfaces with polymer material
2. To focus on superhydrophobic fibrous polymers since fibers present many practical applications
3. To produce superhydrophobic surfaces with hydrocarbon conducting polymers
4. To evaluate the influence of chemical and physical part onto the wetting properties
5. To compare hydrocarbon conducting polymers with fluorinated analogues
6. To study the impact of the polymerizable core onto the properties.

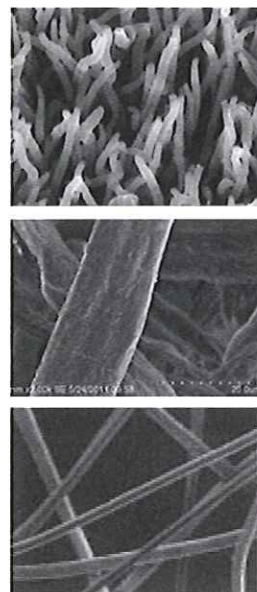
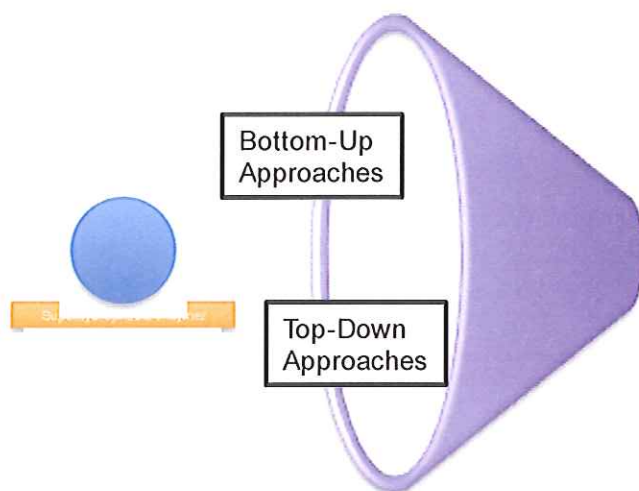
All these challenges can be summed up in Figure 2.

This work is thus divided into four chapters. First, we will present a review of the techniques employed to obtain superhydrophobic polymers then superhydrophobic fibrous polymer surfaces. The second chapter is devoted to one particular hydrocarbon ethylenedioxythiophene (EDOT) series. We will see if superhydrophobicity could be reached with these polymers and if we can get chemical and physical parts impacting onto the wetting properties. Finally, the fourth chapter will describe the surfaces properties comparison between



hydrocarbon and fluorinated surfaces as well as the influence of polymerizable core onto the resultant surface properties.

Chap. 1

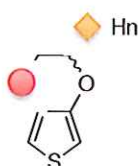


Chap. 2



- Superhydrophobicity with Hydrocarbon conducting polymers?
- % of Chemistry and Physics onto Contact angle?

Chap. 3



- Hn vs. Fn
- Influence of Polymerizable core?

Figure 2. Thesis synoptic representation.